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# IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

**PATENT** 

MICHAEL L. WALKER

Serial No.:

Filed:

For:

Group Art Unit:

BRINE FLUIDS WITH IMPROVED

Examiner:

CORROSION PROPERTIES

Docket No.: 19415337UCIP

: Date: October 11, 2001

# PRELIMINARY AMENDMENT UNDER 37 CFR §1.115

Commissioner for Patents Box Patent Application Washington, D.C. 20231

Sir:

Prior to substantive examination of the subject application, please enter the following response.

#### In the Specification and Claims

Clean Copy of Replacement Paragraphs and Claims – In compliance with new 37 CFR §1.121(c), please find beginning on the next page clean, amended paragraphs and claims. Please substitute and enter these paragraphs and claims for the pending paragraphs and claims with the same number.

I hereby certify that this correspondence, and any attachments referred to, is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to Commissioner for Patents, Box Patent Application, Washington, D.C. 20231, on

OCTOBER 11, 2001

Date of Deposit

David L. Mossman

10.11.2001

Date

New section on page 1, after the title in line 1, and before the heading "Field of the Invention" in line 3:

#### Cross-Reference to Related Application

This application is a continuation-in-part of U.S. Patent Application Serial No. 09/514,825, filed February 28, 2000, now abandoned.

Paragraph appearing on page 2, line 22 to page 3, line 3:

The invention is expected to be useful for any high density fluid having a density of greater than about 8.4 pounds/gallon (1.0 kg/l), preferably from about 8.4 to about 22.5 lbs/gal (1.0-2.7 kg/l), most preferably from about 9.0 to about 22.0 lbs/gal (1.1-2.6 kg/l) and which has low pH, *i.e.*, which is less than neutral. In one non-limiting embodiment of the invention, the density of the high density brine is at least about 11 lb/gal (1.3 kg/l). The salt in the water to make the brine may be a chloride, bromide, formate or acetate salt. The salt cations may be lithium, sodium, potassium, calcium, zinc, ammonium, cesium, and rare earths. Mixtures of salts may also be employed. In one non-limiting embodiment, zinc sources are preferred, and zinc chloride and zinc bromide are particularly preferred zinc sources. Rare earths have their common definition of one or more of a group of 14 chemically related elements in row 6 of the Periodic Table ranging from lanthanum to ytterbium, inclusive. In one non-limiting embodiment of the invention, the brine may include up to 35 wt.% potassium formate, preferably from 0.1 to 30 wt.%.

Paragraph appearing on page 6, line 29 to page 7, line 2:

Optionally, one or more conventional corrosion inhibitors may be used in the brines of this invention to further improve their corrosion properties. In another embodiment of the invention, the additives are used in the absence of other, added corrosion inhibitors. In another embodiment of the invention, the additives are used in the absence of an added Group VB metal (previous IUPAC notation), and particularly in the absence of added arsenic.

#### Claims:

1. (Amended) A corrosion resistant brine fluid comprising:

water;

- a source of water soluble cations where the cations are selected from the group consisting of lithium, sodium, potassium, calcium, zinc, ammonium, cesium, rare earths, and mixtures thereof to form a brine with the water; and
- an additive selected from the group consisting of ammonia, an amine, a salt thereof, a compound capable of generating ammonia, an amine, and a salt thereof, and mixtures thereof where the ammonia, amine, or salt thereof is present in a concentration ranging from about 0.05 to about 2.0 moles of additive per mole of cation, in the absence of added arsenic,

where the density of the brine is at least 11 pounds/gal (1.3 kg/l).

Claim 2 is cancelled.

- 5. (Amended) The corrosion resistant brine fluid of claim 4 where the source of water soluble zinc cations is selected from the group consisting of zinc chloride and zinc bromide.
- 12. (Amended) A corrosion resistant brine fluid comprising:

water;

- a source of water soluble cations where the cations are selected from the group consisting of lithium, sodium, potassium, calcium, zinc, ammonium, cesium, rare earths, and mixtures thereof to form a brine with the water; and
- an additive selected from the group consisting of ammonia, alkyl or aryl amines of the formula R<sup>1</sup>R<sup>2</sup>R<sup>3</sup>N, where R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are independently selected from the group consisting of hydrogen, or hydrocarbon radical or substituted hydrocarbon radical, where the substituent is selected from the group consisting of oxygen, sulfur, nitrogen, halogen and mixtures thereof; where the sum of the number of carbon atoms in R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup>, if

any, is 20 or less; ethylenediamine; aniline; and mixtures thereof, where the additive thereof is present in a concentration ranging from about 0.05 to about 2.0 moles of additive per mole of cation, in the absence of added arsenic;

where the density of the brine is at least 11 pounds/gal (1.3 kg/l).

13. (Amended) A method for increasing the corrosion resistance of a brine fluid comprising:

providing a brine comprising:

water;

a source of water soluble cations where the cations are selected from the group consisting of lithium, sodium, potassium, calcium, zinc, ammonium, cesium, rare earths, and mixtures thereof to form a brine with the water; and

adding an additive selected from the group consisting of ammonia, an amine, a salt thereof, a compound capable of generating ammonia, an amine, and a salt thereof, and mixtures thereof, to provide an additive concentration ranging from about 0.05 to about 2.0 moles of additive per mole of cation, in the absence of added arsenic.

where the density of the brine is at least 11 pounds/gal (1.3 kg/l).

Claim 14 is cancelled.

17. (Amended) The method of claim 16 where in providing the brine the source of water soluble zinc cations is selected from the group consisting of zinc chloride and zinc bromide.

# Version With Markings to Show Changes Made in Paragraphs and Claims

On page 1, after the title in line 1, and before the heading "Field of the Invention" in line 3, please enter the following new section:

# -- Cross-Reference to Related Application

This application is a continuation-in-part of U.S. Patent Application Serial No. 09/514,825, filed February 28, 2000, now abandoned.--

Please amend the paragraph appearing on page 2, line 22 to page 3, line 3 to read as follows:

--The invention is expected to be useful for any high density fluid having a density of greater than about 8.4 pounds/gallon (1.0 kg/l), preferably from about 8.4 to about 22.5 lbs/gal (1.0-2.7 kg/l), most preferably from about 9.0 to about 22.0 lbs/gal (1.1-2.6 kg/l) and which has low pH, *i.e.*, which is less than neutral. In one non-limiting embodiment of the invention, the density of the high density brine is at least about 11 lb/gal (1.3 kg/l). The salt in the water to make the brine may be a chloride, bromide, formate or acetate salt. The salt cations may be lithium, sodium, potassium, calcium, zinc, ammonium, cesium, and rare earths. Mixtures of salts may also be employed. In one non-limiting embodiment, zinc sources are preferred, and zinc chloride and zinc bromide are particularly preferred zinc sources. Rare earths have their common definition of one or more of a group of 14 chemically related elements in row 6 of the Periodic Table ranging from lanthanum to ytterbium, inclusive. In one non-limiting embodiment of the invention, the brine may include up to 35 wt.% potassium formate, preferably from 0.1 to 30 wt.%.--

Please amend the paragraph appearing on page 6, line 29 to page 7, line 2 to read as follows:

--Optionally, one or more conventional corrosion inhibitors may be used in the brines of this invention to further improve their corrosion properties. In another embodiment of the invention, the additives are used in the absence of other, added corrosion inhibitors. In another embodiment of the invention, the additives are used in the absence of

an added Group VB metal (previous IUPAC notation), and particularly in the absence of added arsenic.--

Please amend claim 1 as follows:

--1. (Amended) A corrosion resistant brine fluid comprising:

water;

a source of water soluble cations where the cations are selected from the group consisting of lithium, sodium, potassium, calcium, zinc, ammonium, cesium, rare earths, and mixtures thereof to form a brine with the water; and

an additive selected from the group consisting of ammonia, an amine, a salt thereof, a compound capable of generating ammonia, an amine, and a salt thereof, and mixtures thereof where the ammonia, amine, or salt thereof is present in [an amount effective to raise the pH of and increase the corrosion inhibition of the brine] a concentration ranging from about 0.05 to about 2.0 moles of additive per mole of cation, in the absence of added arsenic,

where the density of the brine is at least 11 pounds/gal (1.3 kg/l).--

Please cancel claim 2.

Please amend claims 5, 12, and 13 as follows:

- --5. (Amended) The corrosion resistant brine fluid of claim 4 where the source of water soluble zinc cations [salt] is selected from the group consisting of zinc chloride and zinc bromide.--
- --12. (Amended) A corrosion resistant brine fluid comprising:

water;

a source of water soluble cations where the cations are selected from the group consisting of lithium, sodium, potassium, calcium, zinc, ammonium, cesium, rare earths, and mixtures thereof to form a brine with the water; and

an additive selected from the group consisting of ammonia, alkyl or aryl amines of the formula R<sup>1</sup>R<sup>2</sup>R<sup>3</sup>N, where R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are independently selected from the group consisting of hydrogen, or hydrocarbon radical or substituted hydrocarbon radical, where the substituent is selected from the group consisting of oxygen, sulfur, nitrogen, halogen and mixtures thereof; where the sum of the number of carbon atoms in R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup>, if any, is 20 or less; ethylenediamine; aniline; and mixtures thereof, where the additive thereof is present in [an amount effective to raise the pH of and increase the corrosion inhibition of the brine] a concentration ranging from about 0.05 to about 2.0 moles of additive per mole of cation, in the absence of added arsenic;

where the density of the brine [ranges from about 8.4 to about 22.5] is at least 11 pounds/gal (1.3 kg/l).--

--13. (Amended) A method for increasing the corrosion resistance of a brine fluid comprising:

providing a brine comprising:

water;

a source of water soluble cations where the cations are selected from the group consisting of lithium, sodium, potassium, calcium, zinc, ammonium, cesium, rare earths, and mixtures thereof to form a brine with the water; and

adding an additive selected from the group consisting of ammonia, an amine, a salt thereof, a compound capable of generating ammonia, an amine, and a salt thereof, and mixtures thereof, to provide [an amount of ammonia, amine, or salt thereof, effective to raise the pH of and increase the corrosion inhibition of the brine] an additive concentration ranging from about 0.05 to about 2.0 moles of additive per mole of cation, in the absence of added arsenic,

where the density of the brine is at least 11 pounds/gal (1.3 kg/l).--

Please cancel claim 14.

Please amend claim 17 as follows:

--17. (Amended) The method of claim 16 where in providing the brine the source of water soluble zinc cations [salt] is selected from the group consisting of zinc chloride and zinc bromide.--

The claims remaining in the application are 1, 3-13, and 15-24.

# **REMARKS**

The Applicants would like to thank the Examiner in the parent application for the indication of allowability of claim 23 therein if rewritten in independent form including all of the limitations of the base claim and any intervening claim.

# Previous Rejection Under 35 U.S.C. §102(b) Over Itzhak

The Examiner in the parent application has rejected claims 1-5, 8, 10, 12-17, 20, 22 under 35 U.S.C. §102(b) as allegedly being anticipated by U.S. Pat. No. 4,997,583 to Itzhak.

If the Examiner in the present application would make a similar rejection, the Applicant must respectfully traverse.

Itzhak consistently and always requires the presence of an arsenic corrosion inhibiting composition. The claims as amended herein specifically recite the absence of added arsenic. Arsenic is notoriously well-known as a carcinogen and a mutagen and thus even those of less than ordinary skill in this art know to avoid it. Since Itzhak does not teach or suggest his compositions and methods in the absence of arsenic, Itzhak does not anticipate or render obvious the amended claims.

It is thus respectfully submitted that an anticipation rejection of the claims has been avoided due to the amendments to the claims. Consideration is respectfully requested.

#### Previous Rejection Under 35 U.S.C. §102(e) Over Mishra

The Examiner in the parent application has rejected claims 1-3, 6, 10-15, 18, 22 and 24 under 35 U.S.C. §102(e) as allegedly being anticipated by U.S. Pat. No. 5,891,225 to Mishra, et al.

If the Examiner in the present application would make a similar rejection, the Applicant must respectfully traverse.

Mishra, et al. is consistently and always concerned with applying halide brines to surfaces requiring protection against freezing conditions (Abstract). Mishra, et al. is not concerned with high density brines, and high density brines are not mentioned therein. All of the claims herein have been amended to require that the brines are high density brines having a density of at least 11 pounds/gallon. Mishra, et al. do not teach or suggest the use of the claimed additives in high density brines as defined herein such as are used in oilfield applications and hydrocarbon recovery, *e.g.* 

It is thus respectfully submitted that an anticipation rejection of the claims based on Mishra, et al. has been avoided due to the amendments to the claims. Consideration is respectfully requested.

#### Previous Rejection Under 35 U.S.C. §102(e) Over Beazley, et al.

The Examiner in the parent application has rejected claims 1-3, 6, 8, 12-15, 18, and 20 under 35 U.S.C. §102(e) as allegedly being anticipated by U.S. Pat. No. 5,935,487 to Beazley, et al.

If the Examiner in the present application would make a similar rejection, the Applicant must respectfully traverse.

Beazley, et al. is consistently and always also concerned only with deicer compositions (Abstract; Background, col. 1, lines 12, et seq.; Summary of the Invention, col. 1, lines 55-63, and elsewhere). Beazley, et al. is not concerned with high density brines, and high density brines are not mentioned therein. All of the claims herein have been amended to require that the brines are high density brines having a density of at least 11 pounds/gallon. Beazley, et al. do not teach or suggest the use of the claimed additives in high density brines as defined herein such as are used in oilfield applications and hydrocarbon recovery, e.g. While calcium chloride brines are mentioned as used to prepare drilling muds and refrigeration brines (col. 4, lines 16-20), there is no teaching or suggestion in these sentences that the brines are high density brines as defined herein.

It is thus respectfully submitted that an anticipation rejection of the claims based on Beazley, et al. has been avoided due to the amendments to the claims. Consideration is respectfully requested.

#### Previous Rejection Under 35 U.S.C. §102(e) Over Johnson, et al.

The Examiner in the parent application has rejected claims 1, 3, 6, 8, 10, 13, 15, 18, 20, and 22 under 35 U.S.C. §102(e) as allegedly being anticipated by U.S. Pat. No. 5,939,362 to Johnson, et al.

If the Examiner in the present application would make a similar rejection, the Applicant must respectfully traverse.

Johnson, et al. is consistently concerned with inhibiting corrosion of iron and steel alloys in contact with oil-in-brine emulsions, particularly of a crude oil (Abstract; claims, and elsewhere). Johnson, et al. is not concerned with high density brines, and high density brines are not mentioned therein. All of the claims herein have been amended to require that the brines are high density brines having a density of at least 11 pounds/gallon. Johnson, et al. do not teach or suggest the use of the claimed additives in high density brines as defined herein such as are used in oilfield applications and hydrocarbon recovery, *e.g.* 

It is thus respectfully submitted that an anticipation rejection of the claims based on Johnson, et al. has been avoided due to the amendments to the claims. Consideration is respectfully requested.

# Previous Rejection Under 35 U.S.C. §102(b) Over the Derwent Abstract

The Examiner in the parent application has rejected claims 1-3, 6, 9, 10, 12-15, 18, 21, and 22 under 35 U.S.C. §102(b) as allegedly being anticipated by the Derwent Abstract of JP 63-199278 A (1988).

If the Examiner in the present application would make a similar rejection, the Applicant must respectfully traverse.

The Derwent Abstract is consistently concerned with reducing corrosion of aluminum in contact with refrigerator brines. The Derwent Abstract is not concerned with high density brines, and high density brines are not mentioned therein. All of the claims herein have been amended to require that the brines are high density brines having a density of at least 11 pounds/gallon. The highest density brine mentioned in the Derwent Abstract has 29.9 wt.% CaCl<sub>2</sub>, which is approximately equivalent to 10.8 lb/gal, which is

below the claim threshold. The Derwent Abstract does not teach or suggest the use of the claimed additives in high density brines as high or higher than those defined herein such as are used in oilfield applications and hydrocarbon recovery, *e.g.* 

It is thus respectfully submitted that an anticipation rejection of the claims based on the Derwent Abstract has been avoided due to the amendments to the claims. Consideration is respectfully requested.

#### Previous Rejection Under 35 U.S.C. §102(b) Over Gipson

The Examiner in the parent application has rejected claims 1, 3, 6, 13, 15, and 18 under 35 U.S.C. §102(b) as allegedly being anticipated by U.S. Pat. No. 3,872,116 to Gipson.

If the Examiner in the present application would make a similar rejection, the Applicant must respectfully traverse.

Gipson is primarily concerned with certain new aminoalcohols and their preparation (Abstract; claims, and elsewhere). Gipson is not concerned with high density brines, and high density brines are not mentioned therein. All of the claims herein have been amended to require that the brines are high density brines having a density of at least 11 pounds/gallon. Gipson only briefly tests some of his aminoalcohols in low density brines (col. 10, lines 36-45). Gipson does not teach or suggest the use of the claimed additives in high density brines as defined herein such as are used in oilfield applications and hydrocarbon recovery, *e.g.* 

It is thus respectfully submitted that an anticipation rejection of the claims based on Gipson has been avoided due to the amendments to the claims. Consideration is respectfully requested.

# Previous Rejection Under 35 U.S.C. §102(b) Over Valone

The Examiner in the parent application has rejected claims 1, 3, 8, 10, 13, 15, and 22 under 35 U.S.C. §102(b) as allegedly being anticipated by U.S. Pat. No. 4,867,888 to Valone.

If the Examiner in the present application would make a similar rejection, the Applicant must respectfully traverse.

Valone is concerned with water soluble or water-dispersible corrosion inhibiting solutions containing ethoxylated, propoxylated alkylphenol amines (Abstract; claims, and elsewhere). However, although Valone mentions brines, Valone is not concerned with *high density* brines. The brine stock Solution A noted in column 8, lines 23-30 of 468 g NaCl, 121.5 g CaCl<sub>2</sub>·H<sub>2</sub>O, and 9722 ml of deionized water gives a brine with a density of only about 8.6 lbs/gal. All of the claims herein have been amended to require that the brines are high density brines having a density of *at least* 11 pounds/gallon. Valone does not teach or suggest the use of the claimed additives in high density brines as defined herein such as are used in oilfield applications and hydrocarbon recovery, *e.g.* 

It is thus respectfully submitted that an anticipation rejection of the claims based on Valone has been avoided due to the amendments to the claims. Consideration is respectfully requested.

# Previous Rejection Under 35 U.S.C. §102(e) Over Atkinson

The Examiner in the parent application has rejected claims 1-3, 6-8, 10, 12-15, 18-20, and 22 under 35 U.S.C. §102(e) as allegedly being anticipated by U.S. Pat. No. 5,846,450 to Atkinson.

The Examiner finds that Atkinson teaches a brine which comprises formates, such as potassium formate, and which further comprises ammonia and other corrosion inhibitors.

If the Examiner in the present application would make a similar rejection, the Applicant must respectfully traverse.

Atkinson is concerned with an absorbent for use in absorption refrigeration systems, air conditioning systems, heat pumps or dehumidifiers that is primarily a solution of potassium formate. The absorbent is relatively non-toxic. The absorbent is generally water-based but may also be ammonia or methanol. (Abstract; claims, and elsewhere). Contrary to the previous Examiner's assertion, ammonia is not taught as a corrosion inhibitor. Corrosion inhibition is supplied by a monohydric alcohol, a polyhydric alcohol, a triazole compound (not shown to decompose to an amine, ammonia, or an amine salt—

the additive recited in the claims), and/or an alkali metal molybdate (col. 3, lines 50-52). Ammonia is instead used as a polar solvent replacement for water (alternatively methanol may be used), where potassium formate is the primary component. The vapor absorbent is 40% to 70% potassium formate (please see the claims, col. 6, line 66 to col. 7, line 1 and elsewhere), and thus the polar solvent comprises the balance, or 30% in its lower proportion. Thus, if the polar solvent is ammonia, and it is used in the low end proportion of 30%, the molar ratio of ammonia to water soluble cation is approximately 20 moles to 1. All of the claims herein have been amended to recite that the additive is present in a concentration ranging from about 0.05 to 2.0 moles of additive per mole of cation. (Support for this change is present in the application as filed, page 4, lines 28-30, and thus does not constitute an improper insertion of new matter.) Atkinson's proportion of approximately 20 moles to 1 of cation far exceeds this range, by about an order of magnitude. The Applicant notes on page 5, lines 2-4 that "Too much of any additive, such as ammonia, causes a precipitate, which is undesirable." Precipitation may not be a concern of Atkinson. Further, Atkinson does not teach or suggest the use of the claimed additive range as now recited in all of the claims.

It is thus respectfully submitted that an anticipation rejection of the claims based on Atkinson has been avoided due to the amendments to the claims. Consideration of the claims is respectfully requested.

#### Previous Rejection Under 35 U.S.C. §102(b) Over Schroeder, et al.

The Examiner in the parent application has rejected claims 1, 3, 6, 8-15, 18, and 20-22 under 35 U.S.C. §102(b) as allegedly being anticipated by U.S. Pat. No. 4,900,458 to Schroeder, et al.

If the Examiner in the present application would make a similar rejection, the Applicant must respectfully traverse.

Schroeder, et al. is primarily concerned with corrosion inhibiting polyalkylene-polyamine compositions (Abstract; claims, and elsewhere). Schroeder, et al. is not concerned with high density brines, and high density brines are not mentioned therein. All of the claims herein have been amended to require that the brines are high density brines having a density of at least 11 pounds/gallon. Schroeder, et al. only briefly mentions

NACE brines (col. 11, lines 3-9), but these are not taught as *high density* brines. Schroeder, et al. does not teach or suggest the use of the claimed additives in high density brines as defined herein such as are used in oilfield applications and hydrocarbon recovery, *e.g.* 

It is thus respectfully submitted that an anticipation rejection of the claims based on Schroeder, et al. has been avoided due to the amendments to the claims. Consideration is respectfully requested.

It is respectfully submitted that the amendments and arguments presented above overcome any expected rejections. Consideration and allowance of the claims are respectfully requested. The Examiner is respectfully reminded of the duty to indicate allowable subject matter. The Examiner is invited to call the Applicants' attorney at the number below for any reason, especially any reason that may help advance the prosecution.

Respectfully submitted, MICHAEL L. WALKER

Pavid L. Mossman Registration No. 29,570 Attorney for Applicants Telephone No. 915/392-8015 Facsimile No. 915/392-8805

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